III. METHANOL AND HIGHER ALCOHOL SYNTHESIS

Dr Helmut Hanisch and Dr Erich Sackmann, respectively head and engineer of the Organic Division, were interrogated on May 12th.

METHANOL

The converter was of the cold-shot type, with external interchanger. Each forging had an I.D. of 800 mm. and was 12 m high; the internals were made either of pure copper or of copper-covered steel. The catalyst basket had an I.D. of 650 mm. and contained 5 or 6 equal beds, holding a total of 3 M^3 catalyst. The circulating gas rate was about 100,000 M^3/hr, giving an output of 120 T/D crude methanol, containing 4 to 5% H_2O, dependent on the CO_2 content of the gas. The compositions of make-up and circulating gas were

	Make-up gas	Circulating gas
CO_2	1 to 1.5%	
CO	30%	18%
H_2	65 to 68%	
N_2	1 to 2%	10 to 15%
CH_4	0.5 to 1%	

The maximum catalyst temperature was given as 390°C, reached towards the end of the converter.

A sample of the catalyst was obtained; it was in the form of 9 mms pellets and was based on zinc and chromium. No CH_4 formation occurred to any measurable extent.

Plant output was of the order of 12,000 T/month crude. Reciprocating circulators were used, not centrifugal ones as used for ammonia.

Water-free methanol was used instead of ethanol in motor fuels. Purified methanol was used for formaldehyde manufacture and for solvents.

HIGHER ALCOHOLS

The name given to higher alcohols was "iso-butanol", although this was the main and not the only substance synthesized.

The plant used was very similar to that used for methanol synthesis, although the interchanger was a little smaller, having an I.D. of only 500 mm.

The circulating gas rate was only 35,000 m^3/hr, giving an output of 40 T/D crude higher alcohols, containing about 12% iso-butanol.

The composition of the gases was :

	Make-up gas	Circulating gas
CO_2	1 to 15%	3 to 5%
CO	30%	25 to 26%
H_2	65 to 68%	
N_2	1 to 2%	10 to 15%
CH_4	0.5 to 1%	

This higher alcohol circulating gas contained more CO and CO_2 than did methanol circulating gas; CO_2 presumably was produced by reaction between CO and water made in the reaction.

The maximum catalyst temperature was given as 450°C. About 2% methanation occurred. The catalyst was the same as methanol catalyst, but with 2% K_2O added; a sample was obtained.

Plant output was of the order of 12,000 T/month crude, i.e. about 1,400 T/month iso-butanol.

Methanol made up half the crude and after separation it was injected into the inlet of the interchanger and re-passed through the converter, where it was converted into higher alcohols. By using stocks of crude higher alcohols the synthesis plant could be run for some time without make-up gas, using only this crude methanol as feed. Such methanol was difficult to purify on account of the hydrocarbons, mostly olefins, it contained.

The composition of crude was given as :-

50 to 55%	methanol	
22 to 25%	water	
1 to 3%	dimethyl ether	
1 to 2%	n-propanol	
11 to 12%	iso-butanol	
2%	C_5	
2.5%	C_6 and C_7	alcohols, ketones, hydrocarbons, etc.
1 to 2%	C_8 and C_9	
1%	C_{10} up to C_{14}	
1 to 2%	hydrocarbons (yellow oil containing 70% olefins)	

The fraction 110° to 160°C amounted to 3 to 4% and the fraction 160° to 250°C also amounted to 3 to 4%.

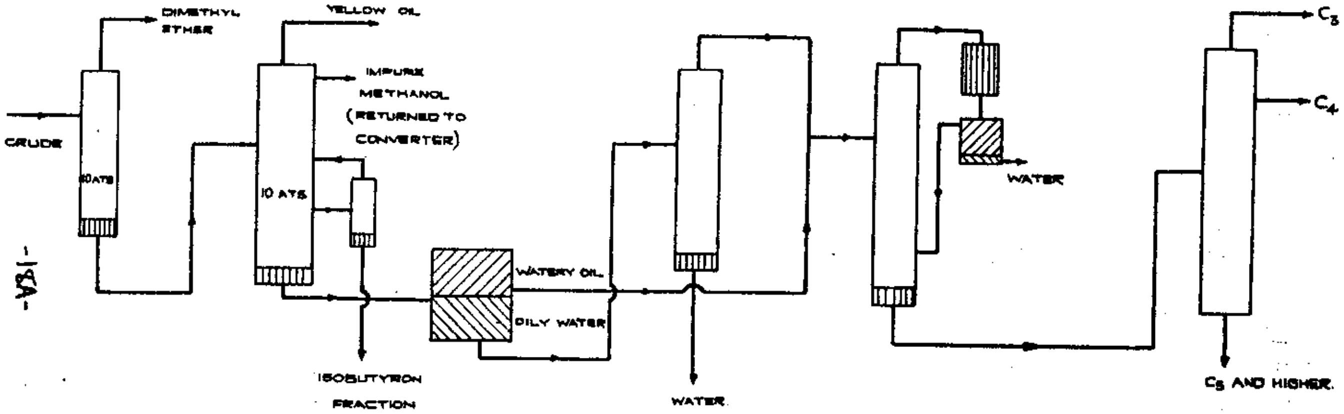
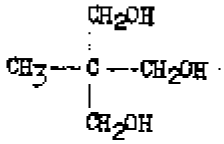


FIG I SEPARATION OF CRUDE HIGHER ALCOHOLS.

The working up of the crude can be followed by reference to Figure I. First dimethyl ether was removed in a ring-packed tower working at 10 ats. Then methanol was removed in a bubble-plate column working at 10 ats; "yellow oil", i.e. the hydrocarbons, was taken overhead and methanol was taken as a side-stream near the top; to obtain an isobutyrone fraction $[(CH_3)_2\ CH.\ CO.\ CH\ (CH_3)_2]$, amounting to 0.5% on crude, a side-still was used as shown. The bottoms from this column separated in two layers; the bottom layer, rich in water, was distilled at 1 at. in a ring packed column to remove water, the overheads being mixed with the top layer, poor in water. Gasoline was added, to form an azeotrope, and the mixture fed to a bubble-plate column operating at 1 at. The overheads from this still on cooling formed two layers; the aqueous one was discarded and the other one was returned to the still. The bottoms from the still were fed to a final bubble-plate column operating at 1 at, with iso-butanol taken off as the main product, propanol taken off overhead, leaving C_5 and greater in the bottoms.

Dimethylether was redistilled in a pressure column and the 98% pure material used for making dimethylsulphate and dimethylaniline.

The propanol fraction was further purified and the purest material was used for cosmetics and in solvents. Other material was converted to propionic acid, but the greater part (100 to 120 T/month) was reacted with formaldehyde to yield trimethylolethane.



$$CH_3 - \overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}} - CH_2OH$$

which when reacted with higher acids (see below) gave a substitute for castor oil. A small amount was also used in the manufacture of glycerine, but this process was carried out to a greater extent at Heydebreck (Upper Silesia) and Oppau, the former using 300 to 350 T/month propanol.

Until July 1944 isobutanol was mostly converted to isobutylene and thence to iso-octane, but then the demand for Oppanol (polyisobutylene) became so great that the butanol was practically all shipped to Oppau and Frose for this purpose. About 80 to 100 T/month were used as acetates as solvents ("Polysolvan") for lacquers; some iso-butylene was used for making butyl phenol at Ludwigshafen, used for lacquer resins. About 80 to 100 T/month were used for making Koresin at Ludwigshafen, a formaldehyde resin. About 100 T/year were converted to isobutylamine.

50 to 60T/month of the fractions 110°-130° and 130°-160° were used as acetates as solvents (e.g. "Intrasolvane"). 400 T/month of the fraction 110°-160° were used to make Palatinol HS, esters of phthalic acid, used as plasticisers.

The fraction 160° to 200° was oxidized to acids and combined with trimethylolethane (see above) to give a substitute for castor oil. The fraction 200° to 250° was used in the manufacture of esters, lubricants and drying aids: the available notes on this are not entirely clear but it appears that the fraction was treated with NaOH and in some way made to yield acids (possibly a naphthenic acid, although this is an obscure reaction), which were then esterified with high alcohols and used as plasticisers or used as Co, Mn or Pb salts as drying aids for lacquers.

Higher fractions could not be used.